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GROWTH AND CHARACTERIZATION OF EPITAXIAL PIEZOELECTRIC AND SEMICONDUCTOR FILMS

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Jul 80

Final Report

For the period 6-1-79 through 7-31-80

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Prepared for the Air Force Office of Scientific Research

Contract No. ██████████

F49620-79-C-0138

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ABSTRACT

This report contains details of the research work
carried out on a one-year project on the growth and charac-
terization of ZnO and AlN piezoelectric thin films. Material
growth systems are reported for ZnO using the zinc vapor
reaction with CO_2, $ZnCl_2$ with O_2, and the latest metal-organic
process. The growth of insulating ZnO has been achieved using
lithium doping during film growth. Initial results are re-
ported for a new AlN growth process that shows promise of
overcoming some previous growth problems.

1.0 INTRODUCTION

This final report is for a one year's effort of an on-going research effort in the growth and characterization of piezoelectric films for use in microwave acoustic devices. The program was basically a continuation of an effort that has been conducted by the PI over the last nine years under the sponsorship of, at one time or the other; JSEP, ONR, AFML, AFCRL (RADC) and most recently AFOSR. The emphasis of the program has shifted according to the demand or interest in unique epitaxial crystal thin films and substrate combinations. The initial work on AlN/Al_2O_3 was prompted by the need for high velocity substrates for microwave SAW delay lines and filters.

During the last two years an increased interest in ZnO for SAW and bulk wave devices has renewed interest in the CVD of this material. Major progress was attained in the CVD of ZnO in the last year through the achievement of high resistivity films of exceptional crystalline quality.

Of major importance to devices is the ZnO film orientation in CVD where the c-axis is in the plane of the film. This configuration allows direct shear wave generation in bulk wave delay lines implying lower propagation losses at microwave frequencies. The high growth rates, ability to dope the film during growth, increased crystal perfection, and potential for wide area coverage suggest that the CVD system will compete with sputtering as a film growth technique.

The report details the recent progress made in the CVD growth of ZnO by a number of techniques. Of considerable interest is the lower temperature growth of ZnO using the metal-organic process. Here excellent films have been obtained at temperatures as low as 400°C. The Zn vapor process using CO_2 has been greatly extended so that now insulating films have been obtained during initial growth. The key to this process has been the incorporation of lithium during growth by a unique vapor transport process. During the year a new growth process for epitaxial AlN was initiated and shows some promise for the growth of this difficult but important material.

The report first gives a general background into the materials and their historical technical problems and then summarizes the results obtained in this project. Details of the research are given in the appendices.

2.0 BACKGROUND

Zinc oxide and aluminum nitride have immense potential for use in the electronics industry. They are wide-band-gap, thermally-stable materials with high piezoelectric coupling coefficients. Layered media in which piezoelectric thin films are hetero-epitaxially deposited on a non-piezoelectric, low loss substrate such as sapphire, have unique properties and applications. These films on R-plane sapphire are of particular interest in this regard because the in-plane c axis orientations allow shear wave generation and are highly compatable with the growth of Si and other materials. Accordingly, numerous attempts have been made to achieve the $(11\bar{2}0)$ 6mm//$(01\bar{1}2)Al_2O_3$ heteroepitaxial system for ZnO and AlN.

2.1 ZnO

Various sputtering techniques have been employed to grow ZnO films with c axis perpendicular to the substrate with varying degrees of success. [1,2] Such films exhibited high resistivity but have the disadvantage of low growth rate and poor crystallinity compared to recent epitaxial films.

Epitaxial films of ZnO can be grown at high rates (100 μm/hr.) by chemical vapor transport or deposition.[3] However, these films are semiconduction, n-type, with an as-grown resistivity of $\approx$ 1 ohm-cm. This value is far too low for devices based on the piezoelectric or electro-optic properties of ZnO where a value of greater than 10^6 ohm-cm

is necessary. Different growth systems have been investigated with the idea that a method yielding high resistivity and film quality may be discovered. However, low resistivity has always resulted and post-growth compensation has been considered to be unavoidable. The low resistivity is attributed to a departure from true stoichiometry of ZnO, with either interstitial zinc or oxygen vacancies acting as the donor. The higher stability of oxygen gas compared to zinc vapor and a difference in the formation energies of Zinc and Oxygen defects make it difficult to grow a stoichiometric crystal. Zinc oxide films are generally grown under low oxygen partial pressure in the presence of hydrogen and are found to be zinc-rich and thus donor-dominated. Even after post-growth lithium doping, the conductivity is still unacceptably high and n-type. It is seen that a moderately high temperature and p_{O_2} (partial pressure of oxygen) must be used in the lithium diffusion process in order to achieve high resistivity.[3] Direct contact of the lithium source (LiOH or Li_2CO_3) is not desirable as it leads to corrosion of both ZnO and the sapphire substrate. The problem of attack has been solved by using vapor transport of lithium by keeping the lithium hydroxide source at a distance from the substrate by the use of a spacer.[4] All attempts to compensate the films are either of inferior quality or polycrystalline. Transport of non-valent metal atoms (eg. Cu, which would lead to compensation) is hard to achieve, and results in drastic morphology

changes when ever successful.

The other problems associated with growth of zinc oxide films are the difficulty of uniform nucleation, poor growth reproducibility and spurious nucleation. Chemosorption properties of ZnO can also become important for films with high surface areas to volume ratio. The surface layers can give rise to depletion layers and influence the defect distribution in the films and change the overall properties of the films. The use of hydrogen as a carrier gas assures low oxygen partial pressure, which promote growth of zinc-rich films, and hydrogen is known to act directly as a donor in ZnO.[5] On the other hand the resistivity of ZnO has been seen to increase in the presence of CO_2. The formation of ZnO by the reaction of zinc vapor with CO_2 has been the subject of studies of formation of ZnO in the Zinc smelting process.[6] The Zn (v) /CO_2 reaction system was recently investigated at USC and resulted in the successful deposition of high resistivity epitaxial films.[7]

High resistivity was exhibited by the as-grown films, which degraded on exposure to atmosphere and handling during interdigital transducer fabrication. This made lithium compensation a necessary step before the films could be used for surface acoustic wave device applications. Compensation of the films during growth by lithium, improvements in the reactor design for better control of the process, and uniform nucleation have now been achieved.

Lithium as a foreign atom in zinc oxide shows

amphoteric behavior. It occupies both the zinc and the interstitial sites where it behaves as an acceptor and a donor respectively. It has been verified that, independent of p_{O_2}, large concentrations of Li always lead to a range in which the concentrations of lithium occupied zinc sites and intersitial sites are equal.[8] Thus lithium saturated samples prepared or treated under moderately oxidizing conditions show high resistivity.[9] Incorporation of lithium during growth has not been achieved by transport using agents such as carbon monoxide or hydrogen. Lithium oxide is a very stable compound and has a low vapor pressure even at high temperatures (10^{-8} mm Hg at $1000^{O}C$). Thus it was found necessary to use a source of lithium oxide close to the substrate, in order to create a sufficiently high partial pressure of lithium oxide over the growing film. This method guarantees the saturation of the ZnO films with lithium, with the result that high as-grown resistivities can be achieved.

2.2 AlN

Aluminum nitride is of interest to microwave acoustic applications because the material exhibits a high SAW velocity of propagation when grown on R-plane sapphire. Although it has the same symmetry and growth habit as ZnO, AlN charactistically grows insulating but at much higher temperatures, $1200^{O}C$.

Details of a new AlN growth procedure are given in the next section.

3.0 PROGRESS

Major emphasis for this past year was on the growth of
insulating ZnO by CVD techniques and the demonstration of a
new AlN growth system. The ZnO work is summarized briefly
below with greater detail left to the appendices. An effort
on planar magnetron sputtering was supported under JSEP at
USC and has given valuable information for any new ZnO
sputtering system.

3.1 Metal-Organic CVD

Epitaxial films have been deposited on sapphire by
using the reaction of diethylzinc with H_2O/H_2 and N_2O/N_2
at temperatures of 400^OC respectively. The results of this
work were presented at the Los Angeles Meeting of the
Electrochemical Society and will be published in the Aug.
1980 issue of the Electrochemical Society Journal. (See
Appendix A)

3.2 $Zn(v)/CO_2$ Process

Excellent quality epitaxial films have been achieved by
using this reaction system (Appendix B). However, the resist-
ivity of these films was low and made lithium diffusion
necessary. This process has now been improved and modified
to incorporate lithium during growth. High resistivity
films can be grown by this process (Appendix C).

3.3 $ZnCl_2/O_2$ System

The zinc-rich nature of the CVD grown films is often
related to the fact that these films are grown under low
oxygen activities. In order to increase the oxygen partial
pressure during growth and use pure oxygen as one of the

components of the reaction system, one must choose a zinc

compound as the other component of the reaction so as to

limit the thermodynamic driving force to a reasonable value.

Zinc chloride with its melting point at $365^{\circ}C$ and boiling

point at $730^{\circ}C$, seems to be the most suitable. Shiosaki,

et at.[10] who studied the $ZnCl_2$-O_2 system, although with a

different motive, found that the system was critically

dependent on the surface treatment of sapphire and always

gave colored films. The color may be related to the fact

that zinc chloride is not available in high purity. The

other problem with $ZnCl_2$ is its deliquescent nature. In

view of this, we employed the reaction of HCl with hot

zinc to produce zinc chloride in situ. An experimental

arrangement similar to the one used for the Zn (v)/CO_2

process was used. 5% HCl in N_2 gas was passed over molten

zinc at $550^{\circ}C$ to produce zinc chloride. Films were grown

at substrate temperatures between $750^{\circ}C$ and $950^{\circ}C$. Although

the continuous films produced on pre-sputtered substrates

showed resistivities higher than 10^6 ohm-cm, the films

showed lack of orientation and high surface roughness. In

general, the growth system was highly irreproducible and

growth rate was limited to 10 μm/hr. It was concluded that

this reaction system was distinctly inferior to the Zn(v)/CO_2

system with lithium incorporation.

3.4   AlN

Chemical vapor deposition appears to be the most

attractive method for fabricating AlN films. CVD provides

good control of growth parameters and a reasonable deposition

temperature of 1200°C. Metal-organic CVD growth using the TMA/NH$_3$ reaction yields good quality epitaxial films at low growth rates. This process is limited to films up to a few microns thickness.[11] The aluminum chloride/ammonia CVD process has been the subject of various studies and appears to be promising for growth at high rates.[12,13] The problems associated with handling extremely hydroscopic AlCl$_3$ have made this process impractical in the past, expecially because very minute quantities of oxygen can give rise to aluminum oxide formation and poor AlN morphology. Thus the use of the HCl and hot aluminum reaction to produce AlCl$_3$ is extremely attractive, but the following problems must be avoided by the careful design of the growth system.

     i)   Formation of AlN at the surface of the aluminum by back diffusion of NH$_3$, which can give rise to a crust of aluminum nitride which would impede the transport of AlCl$_3$.

     ii)   Reaction of AlCl$_3$ with silica which can introduce oxygen into the system.

     A schematic diagram of the growth set-up fabricated is shown in Fig. 1. The system is designed such that the substrate can be taken up to a temperature of 1500°C. The aluminum source is independently heated by a resistance furnace. An aluminum oxide injection tube is used to eliminate the possibility of reaction between AlCl$_3$ and silica. The back diffusion of NH$_3$ to the hot aluminum source should be a minimum in this design. The amount of oxygen and other impurities have to be kept low in this system for the growth of good quality films. Purified H$_2$ and high purity NH$_3$ are
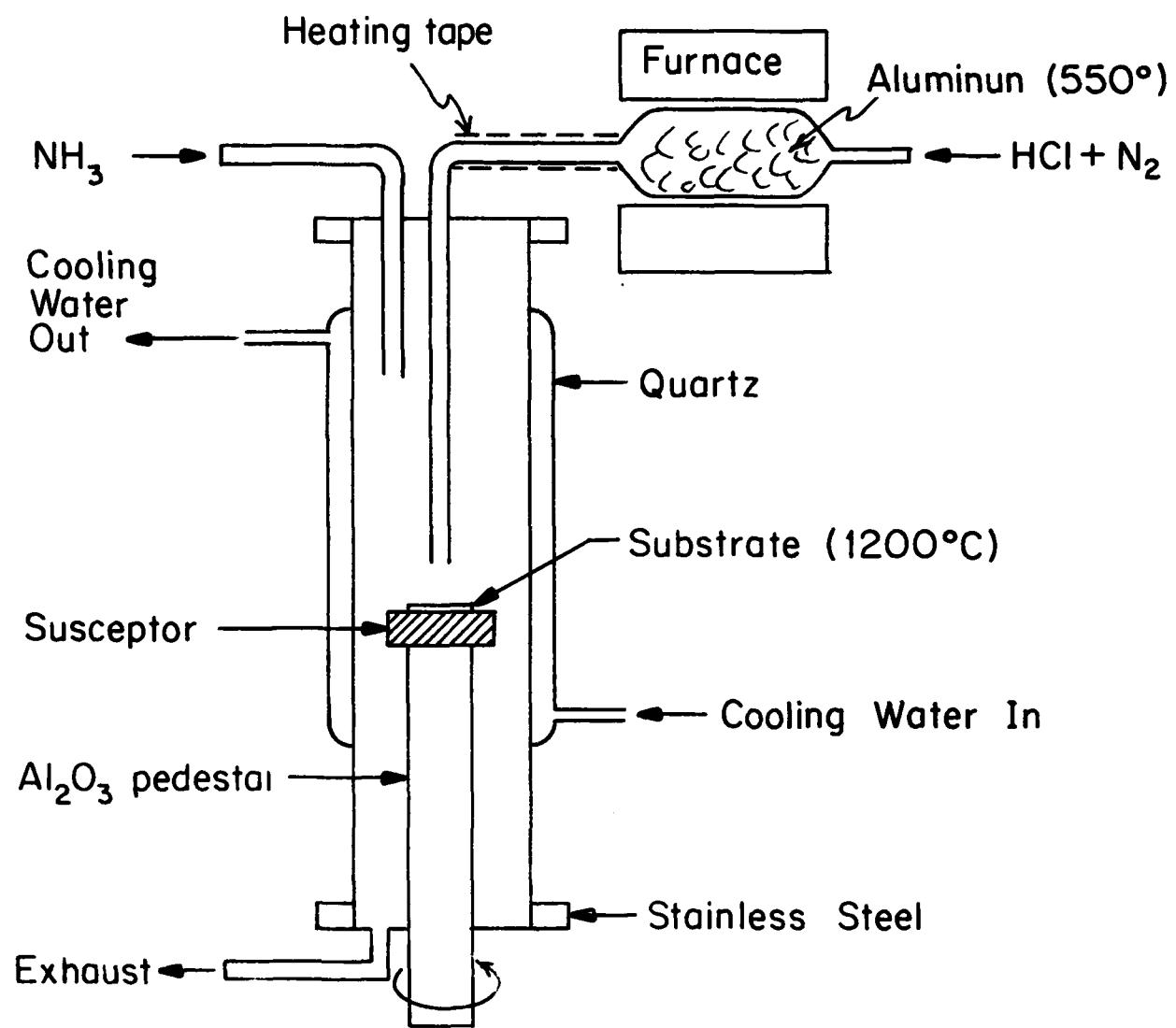
Figure 1. Growth system for the "hot aluminum" process in growing AlN.

therefore used.

3.5 Hydrothermal Growth

Two small research grade hydrothermal autoclaves have been acquired from Leco Corp. of State College, PA. These are LRA 150 RB pressure vessels, and have silver liners. A 3 inch diameter 3 zone vertical furnace has been set up with three temperature controlers, acquired from Eurotherm Corp., used to control the temperature profile of the furnace. The furnace temperature profile has been measured with the pressure vessel in place. Growth runs were not made because of lack of man-power and efforts spent on the more exciting ZnO CVD work.

4.0 SUMMARY AND CONCLUSIONS

During the reporting period considerable progress was made in implementing and understanding the various thin film CVD growth systems. The CVD growth of insulating ZnO has been obtained for the first time using a novel vapor phase doping process and a new growth technique for epitaxial AlN has been introduced.

Because of the unique c-axis in the plane film orientation the ZnO films should be particularly suited to SAW and bulk shear wave devices.

In the future this research effort will be conducted within the Ames Laboratory at Iowa State University.

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Chemical vapor deposition of ZnO epitaxial films on sapphire

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A chemical vapor deposition system for the growth of epitaxial ($11\bar{2}0$) ZnO films on ($01\bar{1}2$) sapphire, employing the reaction of zinc vapor and carbon dioxide, was investigated. Growth rates as high as $30 \mu m/h$ at a substrate temperature of 700-750 °C were achieved. Films grown on substrates with thin presputtered layers exhibited smooth surfaces and improved crystal perfection as determined by SEM, reflection electron diffraction, and acoustic evaluation. Films had high resistivity which eventually degraded on exposure to atmosphere. Surface acoustic wave interdigital transducers were fabricated on lithium-diffused films, and the electromechanical coupling coefficient of 1.39% was measured for a film thickness to wavelength ratio of 0.13.

In the past, ZnO thin films for piezoelectric applications have been grown by sputtering, using techniques that do not yield good quality films at a reasonable growth rate. Recently, planar magnetron sputtering has been successful in producing 10-μm-thick c-axis oriented films on glass substrates within 1 h.[1] Generally, sputtered films have a tendency to grow with the c-axis perpendicular to the substrate surface, although at low growth rates ($10 \mu m/min$) and high substrate temperatures (450 °C), ($11\bar{2}0$) ZnO films on R-plane ($01\bar{1}2$) sapphire can be achieved by magnetron sputtering.[2]

The heteroepitaxial system ($11\bar{2}0$) ZnO on ($01\bar{1}2$) Al_2O_3, with c axis of ZnO in the plane of R-plane sapphire, is highly desirable for surface acoustic wave (SAW) and guided optical wave applications, and vapor phase techniques have been used to achieve this.[3] Using H_2/HCl as transport agents, single crystalline films have been grown at substrate temperatures of 775 °C at growth rates approaching 1.2 μm/min[4] and the H_2/H_2O transport system yields comparable results.[5] Films obtained from the above processes, however, show large surface roughness and low resistivity (1–10 Ω/cm), making postgrowth polishing and lithium diffusion necessary. Moreover, extensive corrosion of the quartz ware occurs immediately downstream from the deposition zone in the H_2/H_2O transport system. This corrosion problem has been eliminated by employing the reaction of water and zinc vapor.[6] In addition, Ohnishi et al. have demonstrated that epitaxial ZnO films with smooth surfaces can be grown by introducing a thin intermediate ZnO layer ($\simeq 13$ nm) on the sapphire substrate by sputtering before chemical vapor deposition[7] The system they used is similar to that of $ZnO/H_2/H_2O$ with the addition of oxygen for enhancing ZnO growth. The growth rate reached 1 μm/min at a substrate temperature of 975 °C. However, an explosion hazard exists in this system and at such a high substrate temperature, the ZnO layer may react with the sapphire substrate. Finally, ZnO films grown in the presence of hydrogen always show high conductivity because of the zinc-rich nature.

In order to solve some of the above mentioned problems, we have investigated the epitaxial growth of ZnO using the oxidation of zinc vapor by carbon dioxide, since film conductivity has been seen to decrease the presence of CO_2.[8]

The schematic diagram of the growth apparatus along with the temperature profile of the furnace is shown in Fig. 1. The growth reaction can be represented by

$$Zn(v) + CO_2 = ZnO + CO.$$

(a)

(b)

FIG. 2. Scanning secondary electron micrograph of a typical as-grown ZnO (a) without presputtering, 1 μm thick, and (b) with presputtering, 4 μm thick.
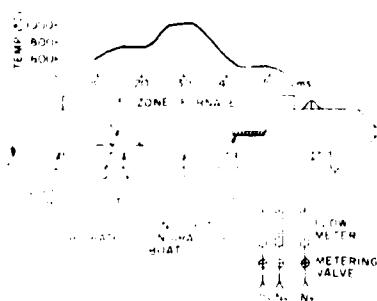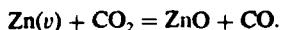
FIG. 1. Schematic diagram of the ZnO system along with the temperature profile of the furnace

Materials used were polished and cleaned (01$\bar{1}$2) sapphire (R-plane) substrates, nitrogen carrier gas obtained directly from liquid nitrogen boil-off, carbon dioxide of 99.999% purity, and zinc shot of 99.999% purity. Typical growth parameters are substrate temperature, 700–750 °C; zinc source temperature, 420–600 °C; center zone temperature, 900–1000 °C; gas flow rates, N_2: 05–2.1 1/min; CO_2: 0.6–4.5 1/min, growth rate, 0.1–0.5 μm/min.

As grown films were transparent with very little roughness and excellent orientation of the surface features, as shown by the scanning electron micrograph of Fig. 2(a). However, initial experiments indicated that the growth tended to be nonuniform over a large area of the substrate, and that growth reproducibility was poor. This indicated that a problem of ZnO nucleation on sapphire exists in this system, as in the case of the other vapor transport systems. It must be born in mind that nucleation and growth in heteroepitaxial systems are different processes, and the same physical or chemical process may not give optimum conditions for both. In order to grow a good epitaxial film, one needs an initial layer which adheres well and is composed of a large number of nuclei per unit area. Planar magnetron rf sputtering was used to grow an initial 10-nm-thick layer of ZnO on the substrate,[7] using the following conditions: target material, ZnO or Zn (12 cm diameter); target-substrate spacing, 4.0 cm; gas composition, 80% Ar, 20% O_2; chamber pressure, 5–10 Torr; rf power, $\approx$ 50 W; substrate temperature, 250 °C; exposure tim, 45 sec.

The sputtering parameters and the nature of the presputtered films were not found to be critical. Subsequent CVD films grown on presputtered substrates were transparent with excellent surface finish suitable for a SAW device. Scanning electron micrograph of a typical as-grown film using sputtered film for nucleation is shown in Fig. 2(b). The films were single crystalline with (11$\bar{2}$0) ZnO||(01$\bar{1}$2) Al_2O_3 epitaxial relationship as confirmed by reflection electron diffraction as shown in Fig. 3.

The resistivity of the as-grown films was higher than those obtained from other CVD processes, and reached 10^6
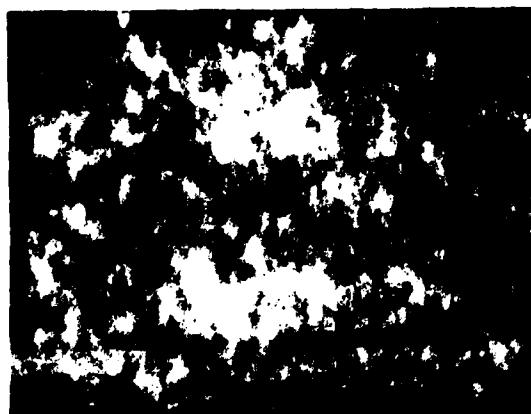
FIG. 4 Impedance plot for 15-μm wavelength IDT on a 1.9-μm-thick lithium-diffused ZnO film on sapphire

Ω cm on some samples. Resistivity, however, degraded on exposure to atmosphere at a faster rate than sputtered films,[2] and lithium diffusion was found to be necessary to hold the resistivity at 10^6 Ω cm or better.

In order to evaluate the electromechanical coupling coefficient, interdigital transducers (IDT) were fabricated on the films using the "lift-off" technique.[8] Figure 4 shows the impedance of a 15-μm-periodicity IDT on a 1.9-μm-thick ZnO film grown at 12 μm/h growth rate. The film thickness to wave length (h/λ) ratio of 0.13 is below the cutoff of all higher-order modes and corresponds to the local maximum value of the electromechanical coupling coefficient k^2.[9] The k^2 value determined from the radiation resistance is 1.39%, which is higher than that obtained for the ZnO/H_2/HCl transport process ($\approx$0.9%)[9] and compares well with the theoretical calculation.[10]

In conclusion, the $Zn(v)/CO_2$ CVD process for epitaxial growth of (11$\bar{2}$0) ZnO on (01$\bar{1}$2) sapphire is superior to other processes in yielding excellent films at a high growth rate for SAW and bulk mode shear wave applications, because of its simplicity, ease of operation, and moderate substrate temperature. Smooth surface finish and excellent reproducibility can be guaranteed using the presputtering technique. By proper use of doping during growth, passivation and handling techniques, the high as-grown resistivity may be used to advantage. Conditions for optimum growth rate, normal c-axis orientation on other substrates, lower temperature growth, and doping during growth are still under investigation.

FIG. 3 Reflection electron diffraction pattern of ZnO on R-plane sapphire using 125-kV electron beam at grazing angle incidence.

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APPENDIX B

Growth of Epitaxial ZnO Thin Films by Organometallic Chemical Vapor Deposition

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ABSTRACT

Organometallic chemical vapor deposition of ZnO on sapphire, using the reaction of diethylzinc with H_2O/H_2, N_2O/N_2, and CO_2/H_2 oxidizing gas systems, has been studied. Epitaxial films have been achieved at temperatures of 400 and 730 C, respectively, in the first two systems. The films have been characterized using scanning electron microscopy (SEM), reflection electron diffraction (RED), and surface acoustic wave techniques.

ZnO is one of the most versatile and useful thin film materials for acoustoelectric, acousto-optic, electro-optic, and photoconductive device applications [1]. The heteroepitaxial system, $(11\bar{2}0)$ ZnO//$(01\bar{1}2)$ Al_2O_3 with the c-axis of ZnO in the plane of the R-plane sapphire, is highly desirable for surface acoustic wave (SAW) device applications because of the high electromechanical coupling coefficient of ZnO and low acoustic wave propagation loss of sapphire. Furthermore, R-plane sapphire is the orientation used in silicon-on-sapphire (SOS) technology and for the growth of many III-V and II-VI compounds, implying the potential for integrating ZnO and semiconductor devices on a single substrate. Finally, substrates with good epitaxial quality surfaces are available commercially.

Growth methods.—RF sputtering, the most popular technique for ZnO thin film fabrication and recently planar magnetron sputtering has been successful in producing 5-10 micron thick films on glass substrates in an hours growth time (2, 3). These sputtered films have a tendency of growing with c-axis perpendicular to the substrate surface and only at very low growth rates (100 Å/min) and high substrate temperatures (~100 C) have $(11\bar{2}0)$ ZnO films on R-plane sapphire been achieved by sputtering (4). Growth of ZnO from the vapor phase has also been widely investigated. Most of the methods reported to date are essentially based on ZnO transport using the transport agents H_2/HCl (5) and H_2/H_2O (6) or con-

trolled oxidation of zinc vapor. Growth rates of about 1.2 μm/min have been achieved at substrate temperatures around 775 C. However, because of the nucleation problems associated with the use of zinc vapor, film growth is nonuniform and nonreproducible. This problem can be solved by the introduction of a pre-sputtered layer of ZnO on the substrate. Using this technique with the $ZnO/H_2O/O_2/H_2$ transport system, Ohnishi *et al.* (7) have grown films with excellent uniformity and surface finish. Growth rates of 1 μm/min were achieved at a rather high substrate temperature of 950 C. However, extensive corrosion of the quartzware takes place in all these transport systems. The corrosion problem has been mitigated by employing the reaction of zinc vapor and H_2O (8).

ZnO films grown by any of the vapor phase techniques show low resistivity, making postgrowth compensation necessary. Diffusion of lithium (and polishing to remove the damage due to etching by the lithium source) must be done before the films can be used for piezoelectric applications. Since the resistivity of ZnO films has been seen to increase in the presence of CO_2 (1), the $Zn(v)/CO_2$ reaction was recently investigated for the growth of ZnO films on sapphire (9). Here an as-grown resistivity of 10^6 Ω-cm resulted, but degraded on further process handling and exposure to the atmosphere.

Organometallic growth.—In recent years, the organometallic process for semiconductor thin film growth has received increasing attention, because of certain distinct advantages largely associated with the ease of handling the metal sources (10). Growth of compound

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semiconductor films using organometallic reactions has been reviewed by Manasevit (11) and the heteroepitaxial growth has been successful for a number of III-V semiconductor materials on various oxide substrates (10). The successful growth of II-VI compounds based on zinc has been reported by Manasevit and Simpson (12.. The only organometallic growth method reported for the deposition of ZnO is by the decomposition of zinc propionate and zinc acetyl-acetonate '13) Oriented films were obtained at extremely low growth rates (27 A/m. i) on mica substrates.

In this paper, we report the results on the growth of ZnO thin films in R-plane sapphire, using the oxidation of diethylzinc, $(C_2H_5)_2Zn$ (DEZ), by the three oxidizing ga. mixtures, H_2O/H_2, CO_2/H_2, and NO_2/N_2 (14). Hydrogen, which plays a dominant role in the growth process, was used as the carrier for the H_2O and CO_2 reaction systems and N_2 was used for the DEZ/N_2O system.

Experiment

Growth system.—Both horizontal and vertical quartz tube reactors were used in the present study as shown schematically in Fig. 1. The vertical gas flow system with substrate rotation proved to be advantageous in the DEZ/N_2O growth system, as more uniform films could be grown. In the case of the DEZ/H_2O reaction system, solid ZnO particles were formed on the inside walls of the injection tube. In the vertical geometry, these particles can be blown by the carrier gas onto the substrate, causing spurious growth problems. The horizontal growth system gave better quality films due to the absence of this problem. In both geometries the gas flow was at near normal incidence to the substrate surface. The temperature was monitored by a thermocouple with its tip placed inside a small hole in the susceptor. The injection tube-to-substrate distance was adjustable. The exhaust was connected to a scrubber through a rotary vacuum pump maintaining a pressure of about 400 Torr inside the reaction chamber.

The entire gas flow system for both the horizontal and the vertical reactors was assembled using stainless steel tubing, stainless steel bubblers for DEZ and deionized H_2O, and with provisions made for purging the system with nitrogen. The quartz reaction chamber is 40 mm ID, 40 cm long tube. The susceptors used were 30 mm diam graphite disks capable of holding 20 mm square substrates.

Nitrogen gas was obtained directly from liquid nitrogen boil-off, and H_2, N_2O, and CO_2 were of four-nine purity. Electronic grade DEZ was chilled with melting ice to get better control over its flow rate (The vapor pressure of DEZ at 20°C is 15 Torr.)

Substrate preparation.—R-plane sapphire 3.8 cm diam and 1.23 mm thick) of epitaxial surface quality was purchased from Union Carbide. A standard polishing and cleaning procedure consisted of Syton (Monsanto) polishing for 10 min followed by cleaning with trichloroethylene, acetone, and methanol Deionized water was used for the final wash before the dry nitrogen blow-off.

Experimental procedure.—To start a growth run, the reactor was evacuated and the carrier gas was admitted. The preparatory sequence continued by heating the substrate to the deposition temperature followed by introduction of the oxidizing gas. After about 5 min, growth was initiated by introduction of DEZ and continued for a specified time. After the growth run, the substrate was cooled slowly.

As-grown films were examined visually under an optical microscope and a small portion of the film was etched away with dilute HCl and the remaining film thickness measured across the etched step using a stylus-type profile meter (Dektak). Further physical characterization was carried out using SEM and RED.

Electrical characterization consisted of a four-point probe resistivity measurement followed by capacitance and electromechanical coupling coefficient measurements using a surface acoustic wave interdigital electrode transducer.

Results and Discussion

Reactions.—DEZ is an electron deficient compound with two vacant orbitals. The presence of these vacant orbitals available for bonding explains its high chemical reactivity. Thus, DEZ forms complexes easily with compounds containing free electron pairs. DEZ forms complexes at temperatures near ambient or higher with H_2O, CO_2, and N_2O (15). The reactions of interest in the present study are:

1. DEZ/H_2O/H_2 system (15)

At room temperature, in the gas stream

$$(C_2H_5)_2Zn + 2H_2O = Zn(OH)_2 + 2C_2H_6$$
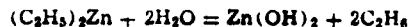
At the surface at high temperature (400°C)

$$Zn(OH)_2 = ZnO + H_2O$$

$$ZnO + H_2 \rightleftharpoons Zn(V) + H_2O$$
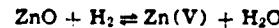
2. DEZ/CO_2/H_2 system (16)

At 150°C, in the gas stream

$$(C_2H_5)_2Zn + CO_2 \rightarrow (C_2H_5COO)_2Zn$$
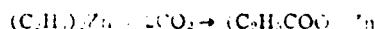
At high temperature, on the substrate (500°C)

$$(C_2H_5COO)_2Zn \rightarrow ZnO + \text{gaseous product}$$

$$ZnO + H_2 \rightleftharpoons Zn(V) + H_2O$$

3. DEZ/N_2O/N_2 system (15)

$$(C_2H_5)_2Zn + N_2O \xrightarrow{\text{low temp.}} \text{"complex"}$$

$$\text{"complex"} \xrightarrow{\sim 700°C} ZnO + \text{gaseous products}$$
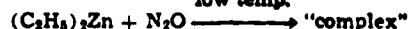
Growth kinetics.—Because of the formation of organo-zinc complexes for $Zn(OH)_2$ in the DEZ/H_2O system at low temperature, it is necessary to keep the reactants separate until they are a short distance
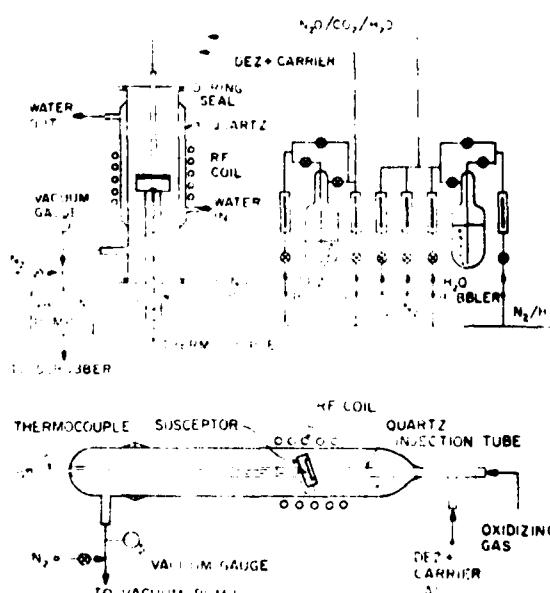

Fig. 1. Schematic diagram of the growth system used for ZnO, OM CVD growth, (a top vertical geometry, b bottom horizontal geometry.

Table I. Growth parameters and properties of ZnO films grown by OM CVD

DEZ N₂O N	710	80 120	2.5	0.21	N₂O .005

Reactor pressure 1 Torr

away from the substrate. Homogeneity of mixing, and uniformity of the reactants uniformly to the substrate is difficult to achieve. The reactor must be geometrically optimized to achieve growth uniformity and low pressure must be used in order to accelerate complex dissociation and removal of reaction products from the growth surface.

Table I shows the growth parameters for the three reaction systems. The rate of growth as a function of
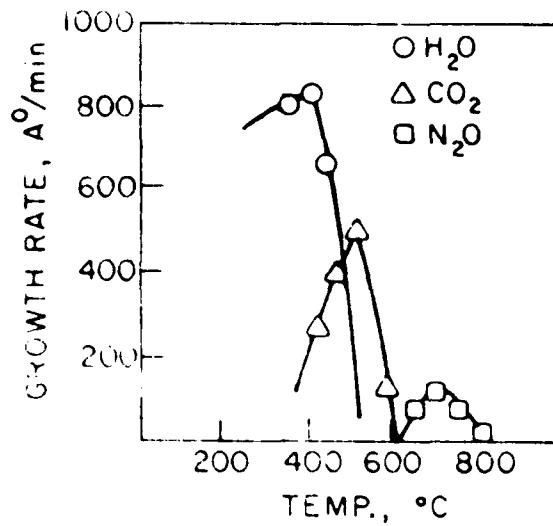
Fig. 2 Growth rate as a function of temperature, with other parameters constant at the optimum values given in Table I.

Fig. 3 Growth rate as a function of ... H₂O, CO₂, and ... in Table I

temperature with all other parameters being maintained equal to the optimum values given in Table I is shown in Fig. 2. The optimum temperatures for the three systems are 400 C for the H₂O/H₂ system, for the CO₂/H₂, and 500 C for the N₂O/N₂ pair. The shapes of the curves indicate that the growth kinetically controlled at low temperature because of the activation energy needed to dissociate Zn(C₂H₅)₂ or the complex. At high temperatures, the growth rate drops due to thermodynamic factors, including the instability of ZnO in the presence of hydrogen. In addition, the growth rate was observed to decrease as the DEZ/oxidizing gas ratio was increased and at very high DEZ concentration growth stopped in all the three reaction systems. This indicated poisoning of the growth surface by excess complex molecules. Thus the desorption of large organic species may be the rate-limiting step under such conditions. Figure 3 shows the dependence of the growth rate on the oxidizing gas flow rate with constant flow rates of other gases equal to the optimum values of Table I. Maxima are observed in each case. Thus adsorption of H₂O, CO₂, and N₂O by the ZnO surface may also lead to a drop in the growth rate.

Growth morphology.—Films obtained with the DEZ/H₂O, H₂ process were pale white translucent with a rough surface. The SEM micrograph for a typical film, shown in Fig. 4, does not reveal any obvious

See attached figure.

Fig. 4 SEM ... for a 2 ... thick ZnO film grown at 400 C by the DEZ/H₂O, H₂ ...

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See attached figure.
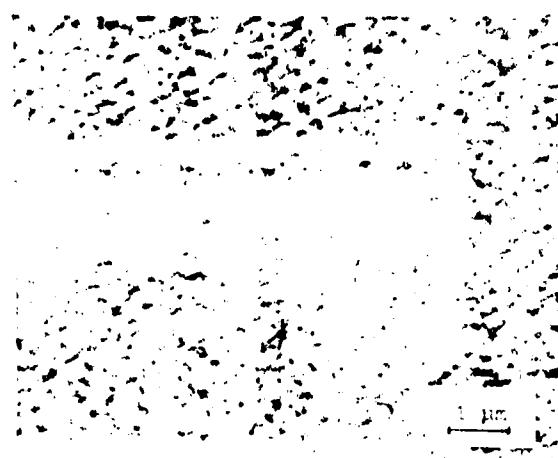
See attached figure.

Fig. 5. SEM/RED for a 2 μm thick ZnO film grown at 500°C by the DEZ/CO₂/H₂ growth system.
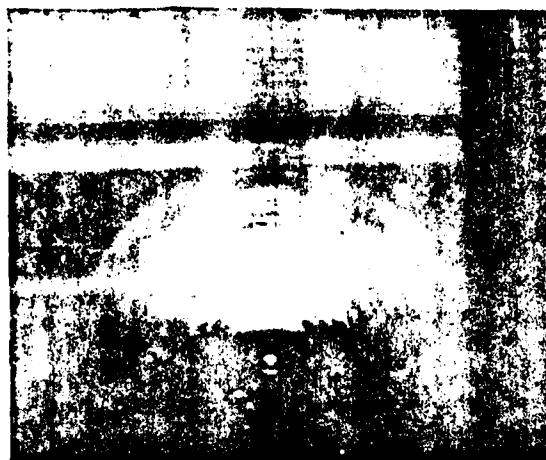
Fig. 6. SEM/RED for a 1.5 μm thick ZnO film grown at 730°C by the DEZ/N₂O/N₂ growth system.

alignment of crystallites, although the RED confirms an oriented film. Films grown by the DEZ/CO₂/H₂ system were polycrystalline (Fig. 5). Films grown by the N₂O/N₂ process were transparent with very smooth surfaces and the SEM/RED data, Fig. 6, show that the crystallites are aligned along the c-axis of ZnO crystallites in the R-plane sapphire. ZnO has a marked tendency of growing fast along the c-axis and it appears that in the presence of H₂ any needles that are not in the growth plane become unstable. In the DEZ/N₂O/N₂ system, because of the absence of hydrogen, spurious growth can become important. Thus, if the arrival rate of the complex is increased by reducing the distance between the injection tube and the substrate, growth rate increases and spurious growth, with hexagonal needles growing out of the plane, is also as shown in Fig. 7. Thus, the growth rate must remain low in order to retain epitaxy.

Electrical characterization.—Resistivity of the films was measured by the four-point probe method. The results are listed in Table II. Films grown by using CO₂ have a high resistivity of 10⁶ Ω-cm and those grown by H₂O and N₂O reactions exhibit low resistivity. For SAW applications, a resistivity of greater than 10⁵ Ω-cm is necessary. Lithium diffusion for increasing the resistivity was carried out for some films, by coating them with Li₂CO₃ solution and heating them at 600°C for 12 hr. The film had to be polished after the diffusion to remove the surface damage due to the etching of Li₂CO₃.
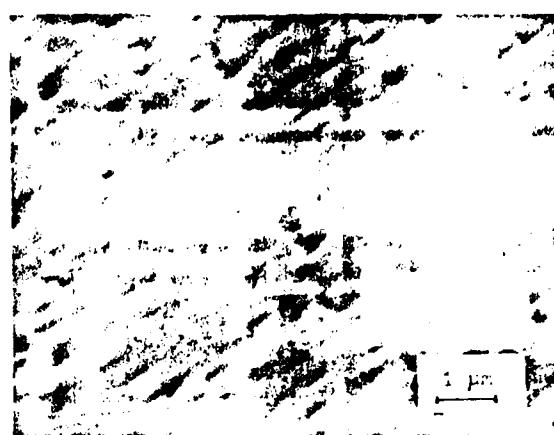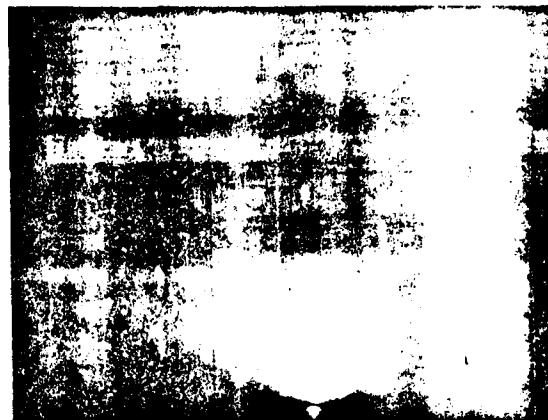
Aluminum interdigital transducers (IDT) of 15 μm wavelength were fabricated on the film surface using the "lift-off" technique (17). The impedance of the IDT was then measured as a function of frequency using an HP8410 network analyzer. The SAW electromechanical coupling coefficient (K²) for the c-axis propagating ZnO/Al₂O₃ structure was then calculated using the expression (18)

See attached figure.

Fig. 7. SEM picture of film grown by the N₂O/N₂ process under high flux conditions, showing spurious growth.

Table II. Properties of ZnO films grown by OM-CVD

Process	Electrical resistivity, Ω-cm		SAW properties				
	As-grown	After Li diffusion	Film thickness,* μm	Resonant freq., MHz	t λ	Coupling coef. K²
DEZ H₂O H₂	1 10	>10⁶	1.0	351.17	0.067	0.22%
DEZ N₂O N₂	10⁻	>10⁶	1.2	343.13	0.08	0.61%

* After polishing, the film thickness was uniform within ±0.1 μm over an area of 1 × 2 cm.

$$K^2 = \pi^2 f_o R_a C_s / 2$$

where f_o = resonant frequency, R_a = radiation resistance, and C_s = capacitance/finger pair.

The coupling coefficient and other relevant parameters are tabulated in Table II. The films grown by the H₂O and N₂O reaction systems were found to be piezoelectric as expected from the RED data. The films grown by the CO₂ process were found to be of poor quality, and several attempts to measure the SAW properties were unsuccessful. For the DEZ/N₂O/N₂ process, a K² value of 0.61% at a thickness to wavelength ratio (t/λ) of 0.08 was determined which is better than the value obtained by Pizzarello using the ZnO/HCl/H₂ closed-space transport process (19), and is comparable to the theoretical value obtained by Lakin and Penunuri (20). The coupling coefficient for films grown by the DEZ/H₂O/H₂ process is lower (0.22% at t/λ = 0.067), but reasonable for a low growth temperature of 400°C.

Conclusion

The organometallic reaction systems using the reaction of DEZ with H₂O/H₂, CO₂/H₂, and N₂O/N₂ were investigated and these show promise as low temperature growth techniques for epitaxial ZnO thin films. The films were evaluated by SEM, RED, and by surface acoustic wave measurements. The films grown by the H₂O and N₂O reactions at temperatures of 400° and 730°C showed electromechanical coupling coefficients of 0.22% at a thickness to wavelength (t/λ) ratio of 0.067 and 0.61% at t/λ = 0.08, respectively.

Methods to increase the growth rate and the resistivity are under investigation.

## Acknowledgment

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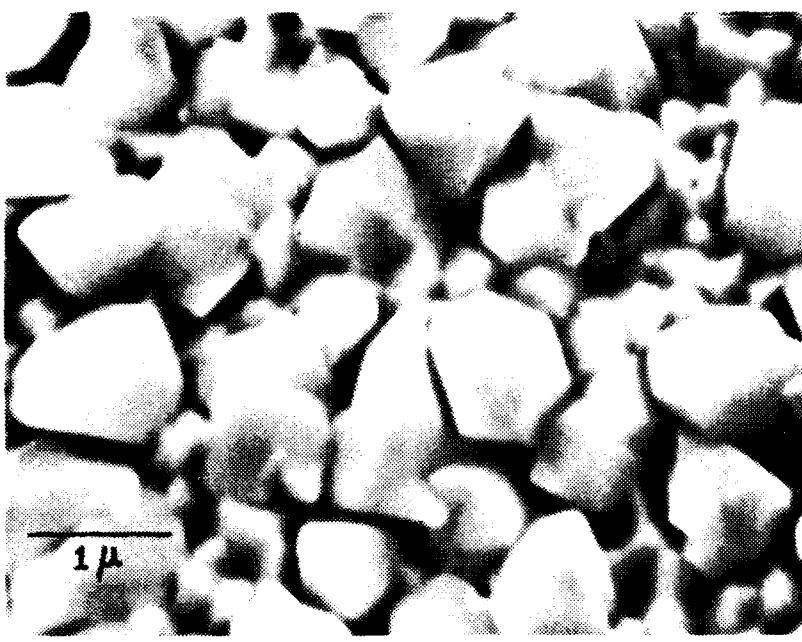
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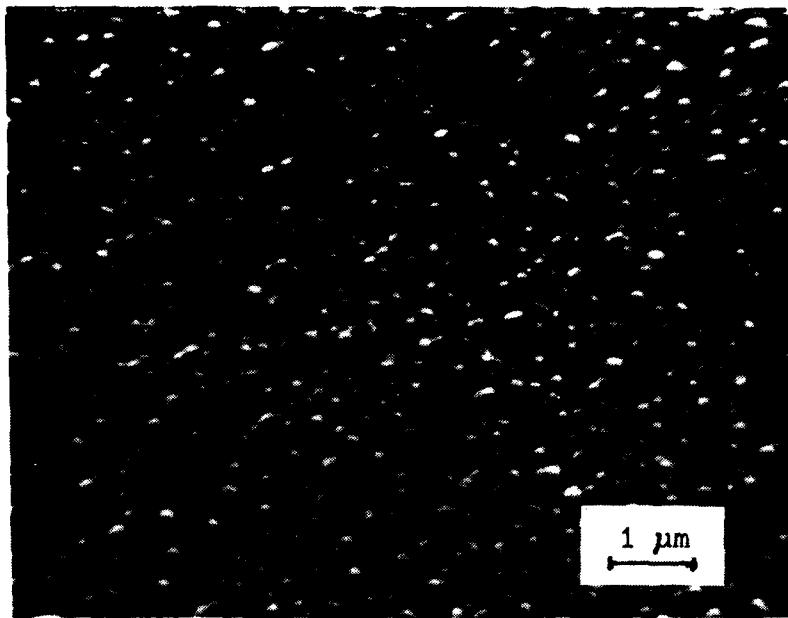
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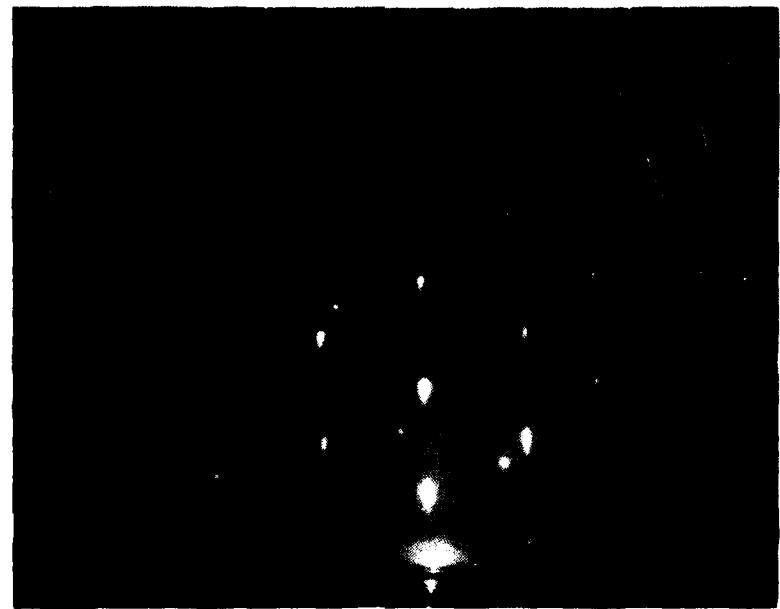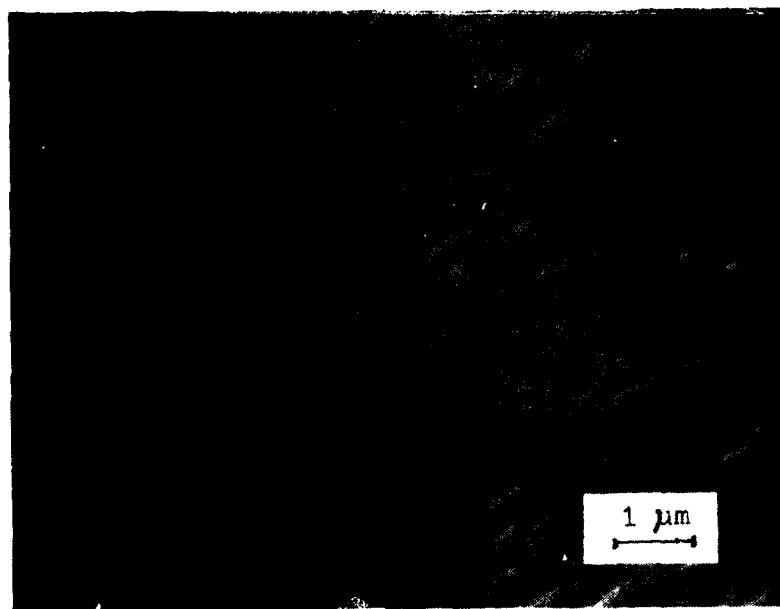
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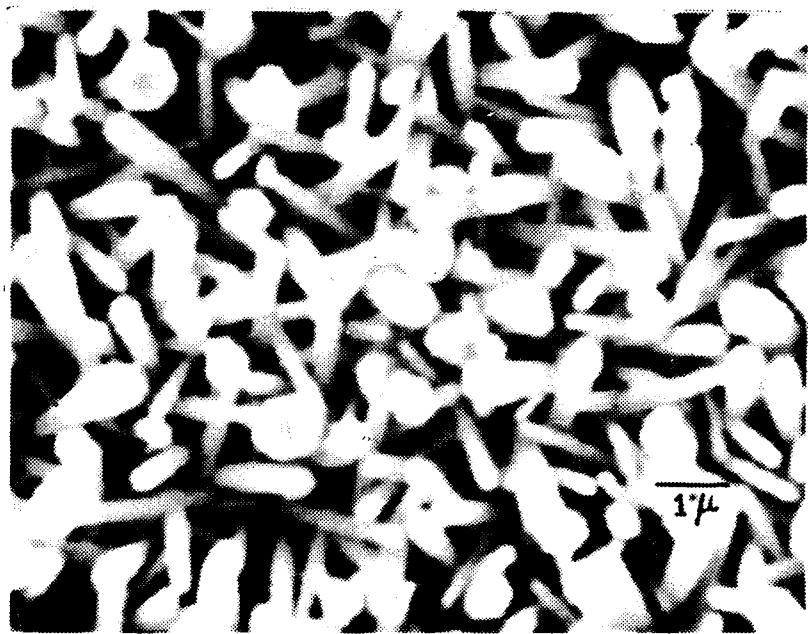
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		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) K. M. Lakin S. K. Tiku		8. CONTRACT OR GRANT NUMBER(s) F49620-79-C-0138 NEW
9. PERFORMING ORGANIZATION NAME AND ADDRESS Electronic Sciences Laboratory University of Southern California Los Angeles, California 90007		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2306/B1 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research Bolling Air Force Base Washington, D. C. 20332 NP		12. REPORT DATE July 1980
		13. NUMBER OF PAGES 24
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
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